

N65-88961  
~~X64 10362~~

14p

THERMOPHOTOTROPISM IN CORTICATED  
ALKALINE EARTH TITANATES

Code 2A

(NAS ATM X-5113)

by  
J. B. Schutt, J. A. Colony, and D. R. Lepp. \*

Goddard Space Flight Center

(TAAG Designs, Inc.)

[1960] 14p 1962 Submitted for Publication

SUMMARY

10362

A comparison of acidic and acidic to basic impurity introduction on the thermophototropic behavior of the alkaline earth titanates is presented. The latter method gave a considerably enhanced absorptivity change for barium titanate, while the identical procedure proved to be much less effective for the titanates of calcium and strontium. In all cases the slurries were made alkaline with alkali metal hydroxides. For barium titanate the optimum alkalinity was obtained with 10 mole percent sodium hydroxide, which led to the conclusion that the phenomenon is a surface one in which the alkali metal oxide corticates the surfaces of the host crystals.

A JTHOR

Available to NASA Offices and  
NASA Centers Only.

## CONTENTS

Summary .....	i
INTRODUCTION .....	1
EXPERIMENTAL .....	3
RESULTS .....	4
TABLE I .....	5
FIG. 1 and 2 .....	6
TABLE II .....	8
TABLE III .....	9
FIG. 3 .....	10
TABLE IV .....	11
DISCUSSION .....	12

**Available to NASA Offices and  
NASA Centers Only.**

# THERMOPHOTOTROPISM IN CORTICATED ALKALINE EARTH TITANATES

by

J. B. Schutt, J. A. Colony, and D. R. Lepp \*

Goddard Space Flight Center

## INTRODUCTION

In the rather large group of photochemically active materials, which have been categorized according to their optical properties, there exist many materials which change color when exposed to light of certain wavelengths. This phenomenon is referred to in its broadest sense as "phototropy."<sup>(1)</sup> The additional property of immediate color reversal with the removal of illumination is usually implied, but is not satisfied, ipso facto, by all phototropes. The alkaline earth titanates (with the exception of magnesium) provide an example; they revert to their original color imperceptibly slowly at room temperature. For example, a decrease of 2 to 3 percent in the absorptivity of barium titanate at room temperature requires approximately three weeks. However, an exposed sample heated to 300°C returns to its original color in about 30 minutes. Therefore, a graph of the functional dependence of coloration on temperature gives a broad curve which extends from about 0°C to several hundred degrees centigrade. Consequently, the alkaline earth titanates are not phototropic in the same sense as organics and metal organics (which bleach at room temperature). Materials such as these are called thermophototropes.

---

\* TAAG Designs, Inc., College Park, Maryland

(1) Chalkley, L., Chem. Rev. 6, 217 (1929)

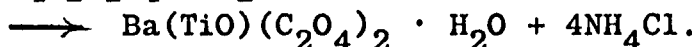
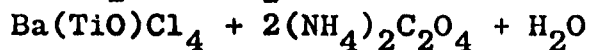
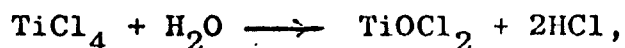
The purpose of this paper is to report a new procedure for the synthesis of a photo-active titanate from a previously synthesized titanate--a procedure which causes a considerably enhanced thermophototropic activity for the barium analog. It is appropriate to briefly mention other possible synthetic approaches. One way is to dissolve the impurity in the form of a salt, usually a chloride, in distilled water and dilute this solution to such a volume that, when slurried with the titanate, a free flowing mixture is formed. Uniform distribution is then assured. A less convenient method involves wet or dry grinding of the impurity with the titanate. Identical procedures are suitable for use with the hydrated titanyl oxalates. Still another technique involves coprecipitation of the impurity with the titanyl oxalate as part of the synthetic procedure.

Since reported observations<sup>(2)</sup> on the thermophototropic behavior of the alkaline earth titanates have been qualitative, the work was repeated in order to establish quantitatively the extent of the photoresponse.

(2) MacNevin, W.M., Ogle, P.R., Jour. Am. Chem. Soc. 76, 3846 (1954).

## EXPERIMENTAL

Initially, impurities were slurried as the chlorides dried, pressed, and fired for one hour at 1100°C. The titanates were synthesized via the oxalate process:



Conversion to the titanate was accomplished at 1100°C in four hours. Previous to firing, the hydrated titanyl oxalate was slurried with  $\text{VOCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{ZnCl}_2$  at a level of 0.02 mole percent. After firing, samples of the titanate were reslurried separately with solutions of elements in the first transition series. Exposures were carried out under a mercury lamp rich in the violet and near ultraviolet energies for 24 hours.

## RESULTS

The results of the spectrophotometric studies are given in Table I for selected wavelengths (the top row listing for each element). In an effort to find a scheme for the incorporation of impurities into the titanates, it seemed appropriate to look for synergisms. Since  $V^{+3,5}$ ,  $Cr^{+3}$ ,  $Fe^{+3}$ , and  $Mn^{+3,-4}$  would be expected to predominately replace  $Ti^{+4}$ , and since  $Co^{+2}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$ , and  $Zn^{+2}$  would be expected to predominately replace the alkaline earth metal, it appeared that synergistic effects could be produced through simultaneous replacement of titanium and barium with cations carrying different ionic charges than that on the cation to be replaced. To this end, the alkali metals were chosen. The results are given in Table I for barium titanate with sodium hydroxide at the 10 mole percent level. They are compared with the corresponding sample prepared without sodium hydroxide. The hydroxide was added by reslurring the doped sample; vanadium was added simultaneously with sodium by means of the pervanadate. Broadly, therefore, Table I is a comparison of impurity activity in an acidic titanate with that in a basic titanate.

In an effort to find out whether the enhanced photoactivity was synergistic, barium titanate was mixed with sodium hydroxide alone. Figure 1 gives the reflectance curves for lithium and potassium as well as sodium from 350 to 700 m $\mu$ . The upper set of curves represent bleached samples and the lower set darkened samples. (In all the figures and tables the alkali metals were added at the level of 10 mole percent unless otherwise stated).

Figure 2 shows replica curves for sodium with barium titanate, after V, Cr, Fe, and Mn had been added to the oxalate as before, and for addition of sodium to the oxalate. Figure 3 is a comparison of additions of sodium in hydroxide and carbonate forms. The enhanced photoactivity found for

TABLE I. A Comparison of Absorptivity Changes for Acidic and Acidic-Basic Impurity Introduction for  $\text{BaTiO}_3$ .

SAMPLE(MOLE %)	400m $\mu$	500m $\mu$	600m $\mu$	700m $\mu$
$\text{V}^{+5}(.02)$	0	2	1	1
$\text{V}^{+5}(.02) + \text{NaOH}(10)$	17	56	49	39
$\text{Cr}^{+3}(.02)$	0	2	1	1
$\text{Cr}^{+3}(.02) + \text{NaOH}(10)$	21	55	54	41
$\text{Mn}^{+3-4}(.02)$	0	$\frac{1}{2}$	$\frac{1}{2}$	1
$\text{Mn}^{+3-4}(.02) + \text{NaOH}(10)$	8	26	32	30
$\text{Fe}^{+3}(.02)$	1	6	4	3
$\text{Fe}^{+3}(.02) + \text{NaOH}(10)$	10	46	53	48
$\text{Co}^{+2}(.02)$	6	4	4	3
$\text{Co}^{+2}(.02) + \text{NaOH}(10)$	6	10	16	25
$\text{Ni}^{+2}(.02)$	0	2	2	1
$\text{Ni}^{+2}(.02) + \text{NaOH}(10)$	23	57	57	50
$\text{Cu}^{+2}(.02)$	2	8	4	0
$\text{Cu}^{+2}(.02) + \text{NaOH}(10)$	10	41	47	40
$\text{Zn}^{+2}(.02)$	0	6	5	4
$\text{Zn}^{+2}(.02) + \text{NaOH}(10)$	11	44	49	39

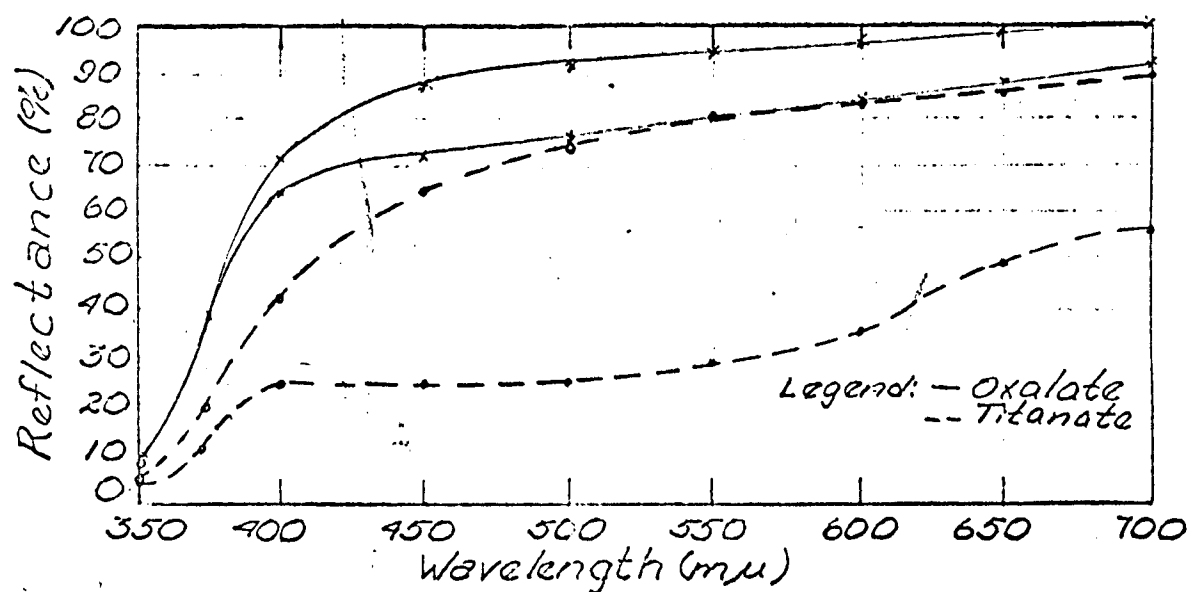


Figure 1. A Comparison of Colorations of Impure Barium Titanate Oxalate and Barium Titanate with 10 Mole Percent of Sodium.

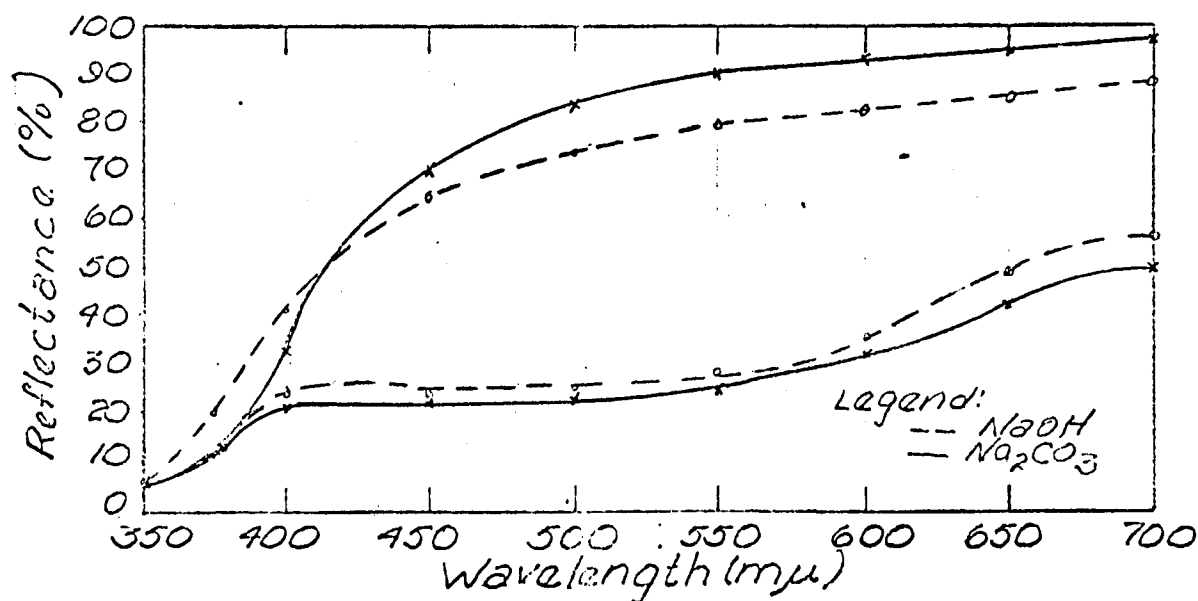


Figure 2. A Comparison of Colorations of Impure Barium Titanate with 10 Mole Percent Sodium Added as Hydroxide and Carbonate.



the carbonate cannot stem from the ease of calcination of sodium carbonate versus the ease of dehydration of sodium hydroxide, since the heat of formation of the former is about twice that of the latter. More likely, the enhancement can be attributed to a lack of decomposition, which gives a relatively dense electron environment.

In an effort to establish an approximate optimum concentration for sodium in barium titanate, the mole percent was varied from 2 to 30 while the samples were fired at  $1100^{\circ}\text{C}$  for one hour. The results are presented in Table II, which shows that 10 mole percent is optimum. With the optimum concentration for sodium, samples were made and fired according to the schedules in Table III. The optimum firing conditions turned out to be 3 hours at  $950^{\circ}\text{C}$  or 1 hour at  $1100^{\circ}\text{C}$ . Under the optimum conditions for sodium addition to barium titanate, samples were made with lithium and potassium additions for comparison with sodium additions. The results are presented in Figure 3. Lithium gave the least response. Sodium and potassium gave similar responses but initially, potassium colored more rapidly than sodium.

Identical synthetic procedures were carried out for calcium and strontium titanates, i.e., V, Cr, Mn, and Fe were added to the respective oxalates and this was followed by repeated additions to the titanate. Following drying the alkali metals were added as hydroxides. Results are given in Table IV. Sodium and potassium increased the overall photo-activity in calcium but did not increase the photo-activity when added to strontium. Lithium inhibited the overall response.

TABLE II. Effect of Na Concentration on the Absorptivity of Impure  $\text{BaTiO}_3$ .

Na(Conc.) - Mole %	Absorptivity Increments (%)			
	400m $\mu$	500m $\mu$	600m $\mu$	700m $\mu$
2	6	30	26	17
5	9	50	47	36
10	15	50	49	37
15	9	55	52	37
20	9	52	51	37
30	8	48	47	35

TABLE III. Effect of Firing Conditions on the Absorptivity Changes of the  $\text{BaTiO}_3\text{-Na}_2\text{O}$  System.

Conditions	Absorptivity Changes (%) at Indicated Wavelengths			
	400m $\mu$	500m $\mu$	600m $\mu$	700m $\mu$
820°C/1 hr.	4	43	37	27
820°C/3 hr.	3	48	44	33
950°C/1 hr.	6	46	43	32
1100°C/1 hr.	7	45	42	31

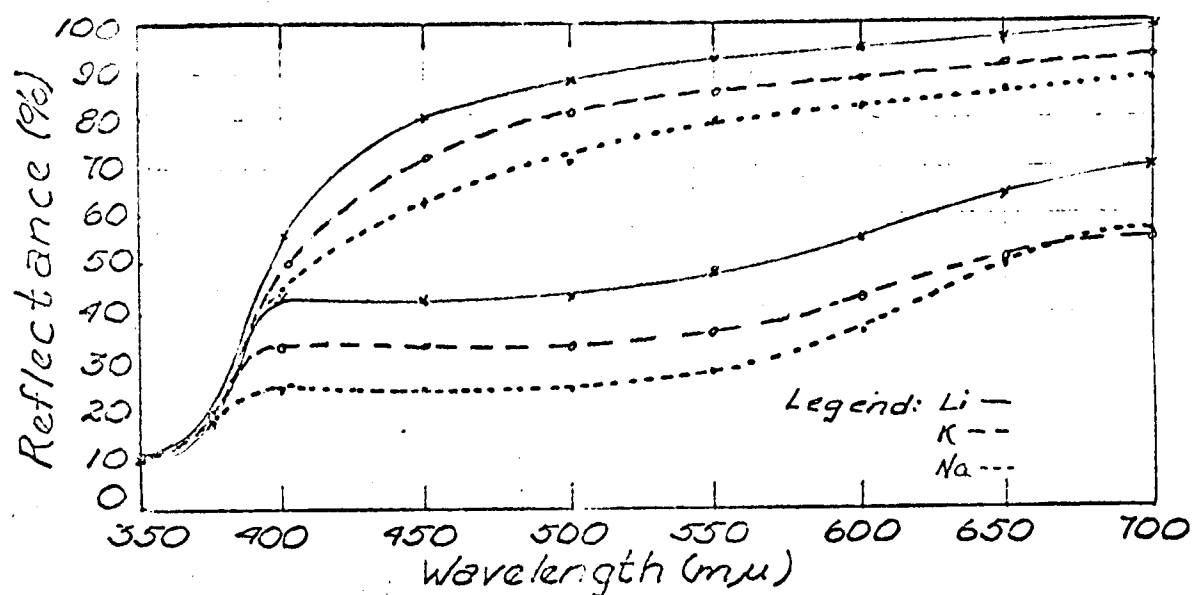


Figure 3. A Comparison of the Colorations of Impure Barium Titanate with 10 Mole Percent Additions of Alkali Metals.

TABLE IV. Absorptivity Changes (%) for Impure  $\text{CaTiO}_3\text{-Na}_2\text{O}$  and  $\text{SrTiO}_3\text{-Na}_2\text{O}$  Systems.

Sample	$\text{CaTiO}_3$				$\text{SrTiO}_3$			
	400m $\mu$	500m $\mu$	600m $\mu$	700m $\mu$	400m $\mu$	500m $\mu$	600m $\mu$	700m $\mu$
Na	8	25	26	23	10	17	14	9
K	6	21	19	14	13	18	15	10
Li	--	--	--	--	9	13	11	8
Impure	6	13	13	9	19	17	14	8

## DISCUSSION

The addition of sodium or potassium ions to impure barium titanate enhances the overall thermophototropic response. Since the level of addition was of such a magnitude that it precluded doping in the semiconductor sense, it seems reasonable to assume that the alkali metals are primarily surface active and do not predominately enter internal lattice positions. Consequently, they corticate the surfaces of the titanate host microcrystals. Lithium gave the least optical response and was temporarily the slowest with respect to rate of coloration. For Potassium, coloration was nearly as great as sodium, and darkening proceeded more rapidly than sodium during the initial stages. Since the ionic radius of potassium,  $1.33\text{\AA}$ , is nearly identical to that of barium,  $1.35\text{\AA}$ , the replacement of barium by potassium is favored over substitution by sodium ( $0.95\text{\AA}$ ). In view of the fact sodium can measurably increase the coloration compared with potassium, it follows that Goldschmidt's Rules are only approximately obeyed for the surface derived phenomenon of thermophototropism.